# ON THE CHEMISTRY OF BIS-SALICYLALDOXIME-Ni(II)

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The solvent and reflectance spectrum of salicylaldoxime as well as of its diamagnetic square planar Ni(II) complex have been investigated.

The electronic spectra of the complex in inert solvents are characteristic of the diamagnetic nickel(II) compounds, while in coordinating solvents the curve is similar to the normal paramagnetic type. From the solutions of the monoamines an adduct of $NiSaOx_2 \cdot L_2$ The $L_2$ can be isolated (L=pyridine, α-picoline, chinoline, n-buthylamine, n-amylamine) with a BM value of 3,16—3,22.

In the mixture of inert and coordinating solvent a diamagnetic/paramagnetic equilibrium forms, the constant of which can easily be calculated from spectroscopic and magnetic data. It was established that the K values and the basic strength of the coordinating solvents change in the same manner.

## *1. Introduction*

A number of square planar, diamagnetic nickel(II) chelates show paramagnetism in indifferent (ID) and in coordinating (CD) solvents with about 0—1 and ~3,2 BM, resp. In the mixture of such solvents a temperature dependent equilibrium develops between the diamagnetic and paramagnetic forms of the complexes, which can be investigated well by various physical and chemical methods.

The purpose of the present investigation was the study of the spectroscopic, magnetic, infrared and equilibrium data of bis-salicylaldoxime-Ni(II).

## *2. General outlines*

With the square planar Ni(II) complexes the singlet $(t_{2g})^6(e_g)^2$ arrangement may lead to strong distortion, since the electron pair on the $d_{z^2}$ orbit repels the ligands situated perpendicular to the $xy$ plane. If the repulsion is strong the two ligands loose their octahedral trans position and a square planar molecule forms [1 – 4].

There are two essential reasons mentioned for the formation of the low spin complexes.

(i) The central metal ion exerts a strong polarization effect on the deformable electrons of the ligands and the overlapping with the $e_g$ orbitals forces the non-bonding electrons of these sub-levels to be paired on the $t_{2g}$ levels.

(ii) The ligands can also form $\pi$-type bonds, while they attract the electrons of the central metal ion, decreasing the repulsion between the $t_{2g}$ electrons.

The Ni(II) is able to form squareplanar chelates only with ligands of significant

[1] SAOx = salicylaldoxime.

field-strength, which are also able to form $\pi$-bonds. The $nd_{x^2-y^2}$, $(n+1)s$, $(n+1)p_x$, $p_y$ orbits play part in the formation of the $\sigma$-bond, while the $(n+1)p_z$ orbit in that of the $\pi$-bond.

The visible spectra of the diamagnetic complexes markedly differ both from those of the octahedral and tetrahedral Ni(II) compounds. It was established [5] that with the square planar arrangement both dia-, and paramagnetic molecules may form. The lowest triplet and singlet state do not separate completely, and there is a point, ($\lambda$), which depends on the field-strength of the ligand and on the value of the effective dipol moment, where the energies of these two states are identical (Fig. 1). Before and after this point the multiplicity of the ground state, the magnetic property of the complexes, as well as the structure of the electronic spectrum are different.

Previously, an equilibrium was assumed in pyridine [6—9] between the non solvated square planar diamagnetic and the solvated octahedral paramagnetic forms. The paramagnetism in ID solvents was interpreted by a square planar →

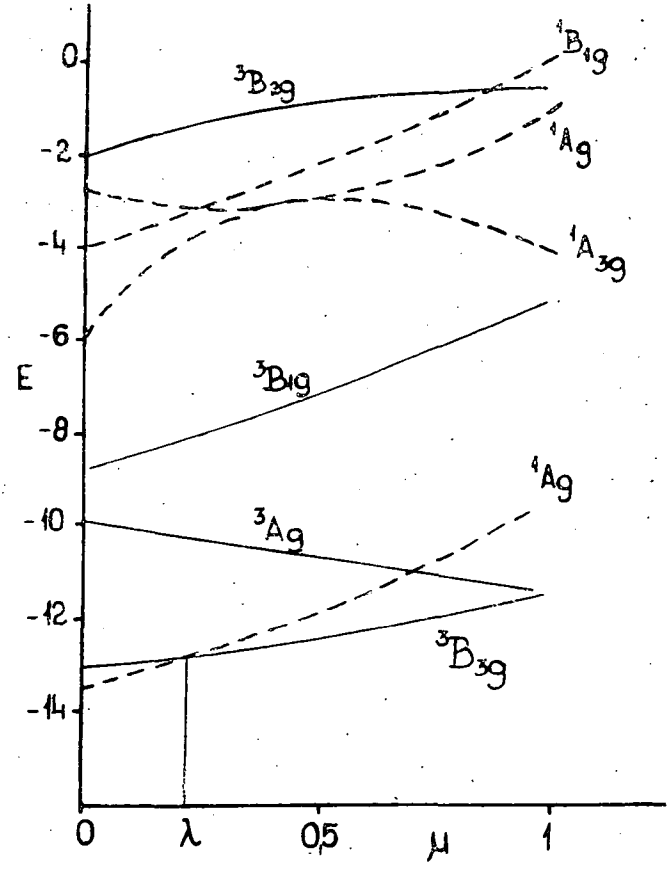



*Fig. 1.* Termsystem of the square planar bis-salicylaldoxime-nickel(II)

→ tetrahedral transformation. According to the group theoretical calculations, in such solvents, an equilibrium exists between the sixfold coordinated high spin molecules and the quadricoordinated low spin ones; the change of the magnetic as well as the spectral properties may also be attributed to the perturbing effect of the solvent molecules.

According to crystal-field calculations the triplet and the lowest singlet state separates considerably in pyridine ($\mu D = 2{,}1$), and the ground state is a purely triplet one (Fig. 1). The energy difference between the $^1A_g$ and $^3B_{3g}$ states is small, therefore, the energy of the heat motion is enough to increase the number of molecules in the higher energy state. Further away from the $\lambda$ point the energy difference can be so great that the BOLTZMANN-factor of the molecules in the greater energy state can be neglected, therefore, a thermal equilibrium does not exist. Before (singlet ground state) and after (triplet ground state) this point the magnetic property and the structure of the spectrum changes considerably.

CLARK and ODELL [10], FUJII and SUMITANI [7], FRENCH ET. AL. [11], BASOLO and MATOUSH [12] and NYHOLM [13] discussed the transformations taking place in solutions. SACCONI ET AL. [14, 15] established the relationship between the equilibrium constants and the base strength of solvents.

The partial paramagnetism of the solid diamagnetic compound in ID solvents can also be caused by the elimination of dimerization [16, 17]. Several authors have been investigating the above mentioned equilibriums, with alkyl- [18—20], sec-alkyl- [21], tercier-alkyl- [22] and also with the aryl- [23, 24] derivatives of salicylaldehyde.

## *3. Experimental data and their interpretation*

### *3.1. Spectroscopical investigations*

#### 3.1.1. *Spectrum of the ligand*

The absorption spectrum of the bidentate SAOx (Fig. 2) measured in alcohol shows bands at 32,680 and 38,610 $cm^{-1}$. For want of quantum mechanical calculations these are, presumably, assigned to the $\pi - \pi^*$ transitions. In acidic solutions the structure of the spectrum is practically unchanged. The formation of a H-bridge

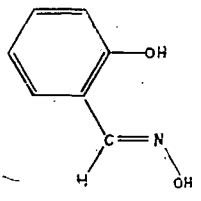



*Fig. 2.*

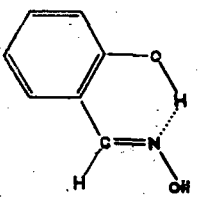



*Fig. 3.*

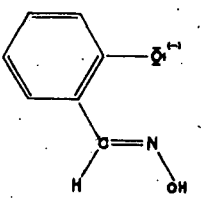



*Fig. 4.*

must be taken into consideration both in alcoholic and acidic media (Fig. 3). In alkaline solutions, because of the formation (Fig. 4) of the phenolate ion, the bands shift considerably towards the long waves. Table I contains the spectral data of SAOx in 10 various solvents.

Table I

Ultraviolet scpectral data of salicylaldoxime in various solvents

| Solvent | Maxima | | | | | |
|---|---|---|---|---|---|---|
| | mμ | kK | log ε | mμ | kK | log ε |
| Water* | 308,0 | 32,47 | 3,44 | 262,0 | 38,17 | 4,03 |
| n-Hexane | 312,0 | 32,05 | — | 264,0 | 37,87 | — |
| $CHCl_3$ | 307,0 | 32,57 | 3,37 | 259,5 | 28,54 | 4,04 |
| Ethanol | 306,0 | 32,68 | 3,57 | 259,0 | 38,61 | 4,04 |
| Dioxane | 305,5 | 32,73 | 3,50 | 258,5 | 38,68 | 3,92 |
| Ether | 305,0 | 32,79 | 3,45 | 259,0 | 38,61 | 4,02 |
| Methanol | 304,0 | 32,89 | 3,39 | 257,5 | 38,83 | 3,80 |
| i-Oktane | 303,5 | 32,94 | 3,46 | — | — | — |
| n-Heptane | 302,5 | 33,05 | 3,47 | — | — | — |
| $CCl_4$ | 301,5 | 33,17 | 3,51 | — | — | — |

* Because of the low solubility the log ε values are uncertain.

3.1.2. *Spectrum of the central ion*

The $^3F$ ground term of the nickel(II)ion [(Ar)$3d^8$] splits into $^3A_{2g}$, $^3T_{2g}$ and $^3T_{1g}$ levels in order of increasing energy in potential field of high symmetry [25—27].

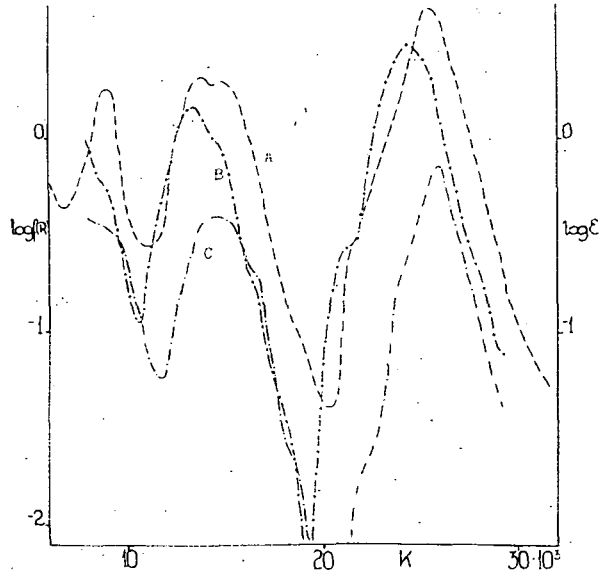



*Fig. 5. A*, solution spectrum of $[Ni(H_2O)_6](ClO_4)_2$; reflectance spectra of *B*, $NiCl_2 \cdot 6\,H_2O$ and *C*, $NiSO_4 \cdot 6\,H_2O$

Taken also the $^3P$ term into consideration in the electronic spectrum of $[Ni(H_2O)_6]^{2+}$ (28—30) and in the reflectance spectra of $NiSO_4 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ the three bands can be assigned to the

$$^3A_{2g}(^3F)[(t_{2g})^6(e_g)^2] \rightarrow {}^3T_{2g}(^3F)[(t_{2g})^5(e_g)^3] \quad (\nu_1)$$

$$\rightarrow {}^3T_{1g}(^3F)[(t_{2g})^5(e_g)^3] \quad (\nu_2) \quad (1)$$

$$\rightarrow {}^3T_{1g}(^3P)[(t_{2g})^4(e_g)^4] \quad (\nu_4)$$

LAPORTE-forbidden transitions (Table II, Fig. 5).

Table II

| $^3A_{2g} \rightarrow$ | $[Ni(H_2O)_6]^{2+}$ mμ | kK | $NiSO_4 \cdot 6H_2O$* mμ | kK | $NiCl_2 \cdot 6H_2O$* mμ | kK |
|---|---|---|---|---|---|---|
| $^3T_{2g}$ | 1176 | 8,5 | 1053 | 9,5 | 1075 | 9,3 |
| $^3T_{1g}$ | 690 | 14,5 | 690 | 14,5 | 752 | 13,3 |
| $^3T_{1g}$ | 395 | 25,3 | 386 | 25,9 | 410 | 24,4 |

* Reflection spectra

3.1.3. *Spectrum of the complex*

The central nickel(II)ion bounds two SAOx in plane (Fig. 6). The bonds form between the O-ion, formed by the dissociation of the alcoholic OH-group, and the N-atoms as well as the central metal ion. According to X-ray investigations [31] an H-bridge exist in the complex, as is found at the oxime complexes. This is shown by the i. r. spectrum of SAOx and that of its nickel(II) complex (Table III). In the i.r. spectrum of the free molecule the wide band of the OH-group appears at 3360 $cm^{-1}$, but this band is not present at the complex. The C=N stretching frequency is found at 1642 $cm^{-1}$, shifted towards the higher wave numbers as compared to the free ligand (1633 $cm^{-1}$). The electronic spectra of the square planar, deep green compounds are shown in Fig. 7, the data are tabulated in Table IV.

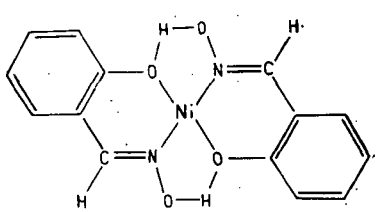



*Fig. 6.*

In the solution spectrum below 380 mμ the characteristic bands of the ligands can be found, while in the visible one sharp band one inflexion appear. This latter section is characteristic of all square planar diamagnetic nickel(II) complexes measured in ID solvents (28). On the analogy of MAKI's assignment this band and inflexion in the reflectance spectrum — which is completely similar to the solution spectra — correspond to the $^1A_{1g} \rightarrow {}^1B_{3g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ transitions, resp. (Fig. 8).

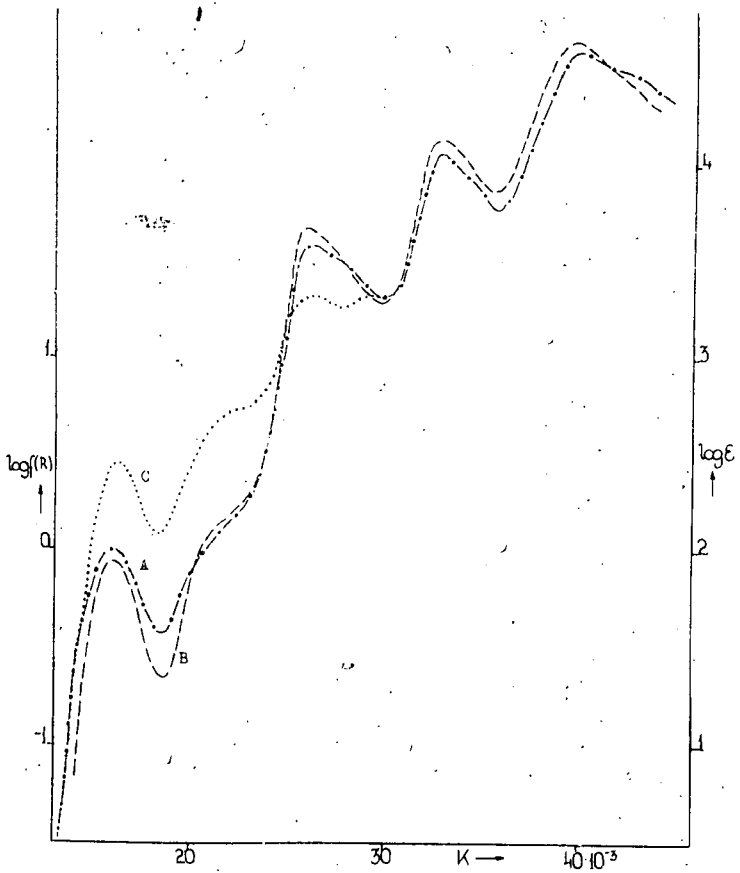



*Fig. 7.* Solution spectra of $NiSAOx_2$ in *A*, $C_2H_5OH$; *B*, $CHCl_3$; *C*, reflectance spectrum

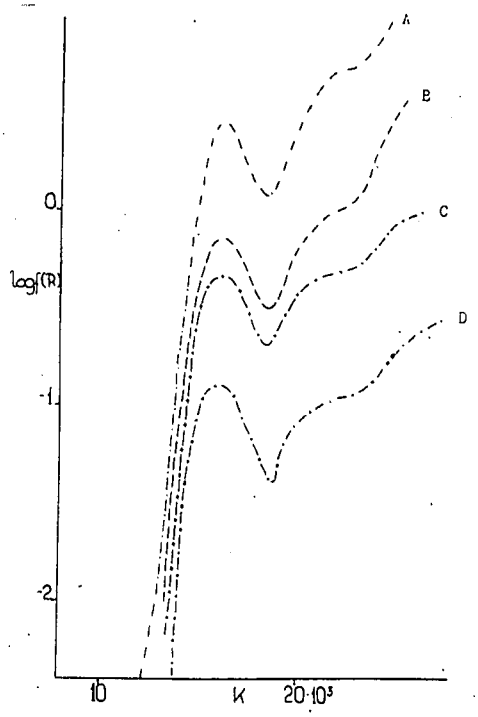



*Fig. 8.* Reflectance spectra of $NiSAOx_2$ with $NiSAOx_2$:MgO = *A*, 1:0; *B*, 0,75:0,25; *C*, 0,5:0,5; *D*, 0,25:0,75

Table III

Infrared band position of salicylaldoxime and of Ni(II) complexes

| SAOx | $NiSAOx_2$ | Assignments |
|---|---|---|
| 420 w | 425 m | |
| 468 m | 468 m | |
| — | 526 w | Ni—O str. |
| 562 m | — | |
| 605 w | 616 m | |
| 647 s | 645 s | |
| — | 672 m | |
| 700 m | 689 m | |
| 724 w | 710 w | |
| 743 m | 754 s | |
| 768 w | — | |
| 790 m | — | |
| 860 m | 824 s | |
| — | 852 w | |
| 904 s | 916 s | |
| — | 947 m | |
| 962 m | — | |
| 994 s | 1022 s | |
| 1042 w | 1047 w | |
| 1118 w | 1124 w | N—O str. |
| 1157 m | 1167 w | |
| 1196 m | 1202 m | |
| 1217 w | 1217 w | |
| 1259 s | 1257 m | C—O str. |
| 1292 s | 1297 s | |
| — | 1341 s | |
| 1416 s | — | |
| — | 1447 s | |
| 1480 m | 1478 s | |
| 1502 s | 1503 m | vibrations of o-subst. |
| 1582 s | 1554 s | benzene |
| 1623 s | 1603 s | |
| 1633 m | 1642 m | C=N str. |
| — | 2950 m | |
| 3360 m | — | str. vibration of phenolic O—H group |

w: weak, m: medium, s: stark, str.: stretching vibration

Table IV

Position of the visible bands of $NiSAOx_2$ in various solvents

| Solvent | Maxima | |
|---|---|---|
| | mμ | kK |
| Ethanol | 626 | 15,97 |
| Propanol | 625 | 16,00 |
| Acetone | 624 | 16,03 |
| $CHCl_3$ | 624 | 16,03 |
| Dioxane | 623 | 15,05 |
| Methanol | 619 | 16,16 |
| $CCl_4$ | 614 | 16,29 |
| Nitrobenzene | 614 | 16,29 |

A considerable change can be observed in CD solvents, such as pyridine, chinoline, picoline or aliphatic amines, *etc.* In these solvents the complex shows paramagnetism with about 3,2 BM and the structure of the absorption curve is similar to the ones of the six-coordinated paramagnetic compounds (Figs. 9 and 10).

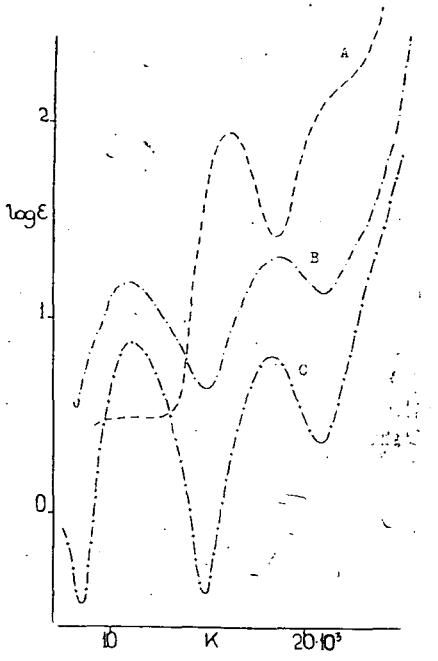



*Fig. 9.* Solution spectra of $NiSAOx_2$ in *A*, $CHCl_3$; *B*, picoline; *C*, ethylenediamine

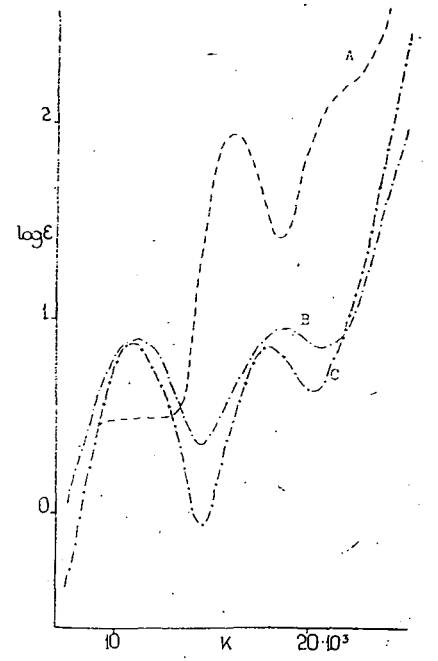



*Fig. 10.* Solution spectra of $NiSAOx_2$ in *A*, $CHCl_3$; *B*, tetraethylene-pentamine; *C*, trimethylene-diamine

The data of the bands of the $^3B_{3g} \rightarrow {}^3B_{1g}$ and $^3B_{3g} \rightarrow {}^3B_{2g}$ transition are tabulated in Table V.

The third band appearing at the border-line of the u.v. region is blurred because of the self-absorption of the solvents. Crystallyzing $NiSAOx_2$ from the above solvents a brownish-violet six-coordinated, normal paramagnetic compound forms. The reflectance spectrum of this adduct is identical with that of the six-coordinated compound, but in solution the solvent molecules split-off and the spectrum shows again the characteristic structure of the green diamagnetic form (Fig. 11).

### *3.2. Equilibrium investigations*

3. 2. 1. *On the basis of extinction measurements*

In a mixture-system of ID and CD solvent the six-coordinated paramagnetic and the square planar diamagnetic modification of the complex form a temperature dependent equilibrium system. With increasing concentration of the CD solvent the intensity of the $^1A_{1g} \rightarrow {}^1B_{3g}$ band of the diamagnetic form will gradually de-

Table V

Visible spectra of $NiSAOx_2$ in aliphatic amines

| Amines | First d-d band | | Second d-d band | |
|---|---|---|---|---|
| | kK | log ε | kK | log ε |
| $CHCl_3$ | 16,03 | 1,96 | 21,00 | — |
| En | 11,00 | 0,88 | 18,30 | 0,81 |
| TMDA | 10,90 | 0,88 | 17,80 | 0,87 |
| PMDA | 10,95 | 1,00 | 17,70 | 0,94 |
| TEPA | 11,10 | 0,90 | 18,60 | 0,96 |
| Pyridine | 10,70 | 0,90 | 18,35 | 1,08 |
| α-Picoline | 10,90 | 1,18 | 18,65 | 1,32 |

En: ethylenediamine, TMDA: trimethylenediamine, PMDA: pentamethylenediamine, TEPA: tetraethylenepentamine

crease and be shifted towards the $^3B_{3g} \rightarrow {}^3B_{2g}$ band of the paramagnetic form. The inflexion around 25,000 $cm^{-1}$ will gradually disappeare.

There is a definite correlation between the intensity of the bands and the CD solvent contrentration. The intensity of the bands increases with decreasing CD solvent contrentration and increasing temperature (Tables VI and VII). From Fig. 12

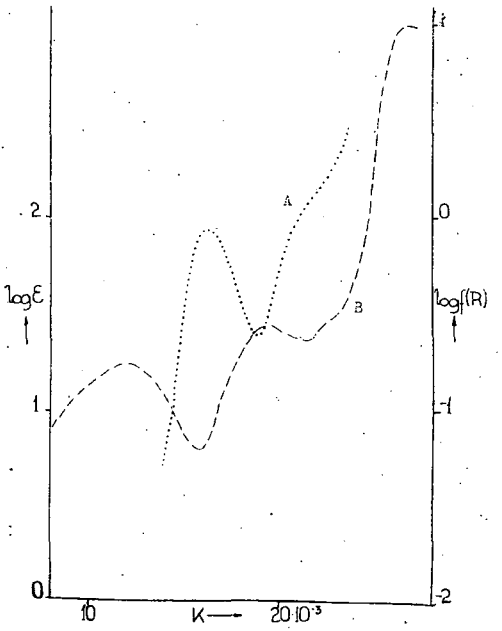



*Fig. 11.* $NiSAOx_2 \cdot 2\,C_5H_5N$. *A*, solution spectrum in $CHCl_3$; *B*, reflectance spectrum

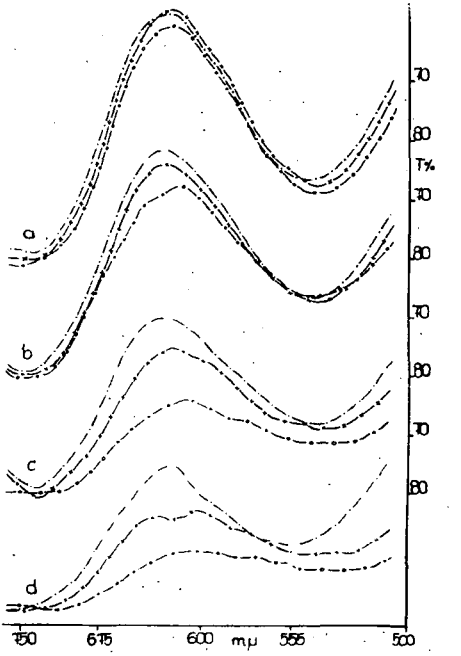



*Fig. 12.* Temperature effect on the spectra of $NiSAOx_2$ in $CHCl_3$—$C_5H_5N$ systems: $cc_{pyridine}$: $a=0$; $b=0{,}036$; $c=0{,}072$; $d=0{,}145$ M; $T=283$ (—·—·—); 298 (—x—x—); 313 K° (—o—o—o—).

Table VI

Visible spectra of $NiSAOx_2$ in $CHCl_3$ in the presence of various pyridine concentration

| $cc_{py}$ (M/l) | log $\varepsilon_{16,000}$ | log $\varepsilon_{21,000}$ | Position * |
|---|---|---|---|
| 0 | 1,96 | 2,10 | 16,03 |
| $4{,}27 \cdot 10^{-2}$ | 1,58 | 1,83 | 16,20 |
| $1{,}24 \cdot 10^{-1}$ | 1,38 | 1,66 | 16,40 |
| $2{,}48 \cdot 10^{-1}$ | 1,03 | 1,36 | 17,80 |
| $4{,}97 \cdot 10^{-1}$ | 0,86 | 1,18 | 18,10 |
| $6{,}21 \cdot 10^{-1}$ | 0,80 | 1,12 | 18,30 |
| in pyridine | 0,76 | 0,93 | 18,30 |

Indicated of the shift of the main bands in Kk

Table VII

Temperature effect on the spectra of the $NiSAOx_2$ in various $CHCl_3$-pyridine systems

| $cc_{py}$ (M/l | T | Maxima | | |
|---|---|---|---|---|
| | | mμ | $cm^{-1}$ | T% |
| 0 | 283 | 615 | 16,260 | 61 |
| | 298 | 615 | 16,260 | 59 |
| | 313 | 615 | 16,260 | 58 |
| 0,036 | 283 | 605 | 16,530 | 69 |
| | 298 | 614 | 16,290 | 64 |
| | 313 | 617 | 16,210 | 62 |
| 0,072 | 283 | 601 | 16,640 | 84 |
| | 298 | 608 | 16,450 | 76 |
| | 313 | 617 | 16,210 | 70 |
| 0,145 | 283 | 595 | 16,810 | 90 |
| | 298 | 605 | 16,530 | 84 |
| | 313 | 611 | 16,370 | 75 |

it can be seen, that with increasing pyridine concentration the change of temperature causes a greater and greater difference in the intensity of the bands; at a higher pyridine concentration also in their position. Thus, the lower is the concentration of the CD solvent and the higher is the temperature the fewer is the number of molecules where the perturbating effect of the solvent molecules comes into account and the equilibrium gradually shifts towards the form of a singlet ground state.

The above mentioned are also supported by Fig. 13, which shows the change of extinction of solutions of identical pyridine concentration *vs.* the temperature. The change is linear and is the greater the smaller is the pyridine concentration. The $\operatorname{tg}\alpha$ of these straight lines also give a linear correlation *vs.* the pyridine concentration.

The equilibrium constants are summarized in Table VIII; the $\log K - 1/T$ relationships are given in Fig. 14. It can be seen that the $K$ values change identically according to the basic strength of the CD solvents. This is in accordance with the findings of SACCONI ET AL. [14]. The α-picoline is an exception, where the methyl

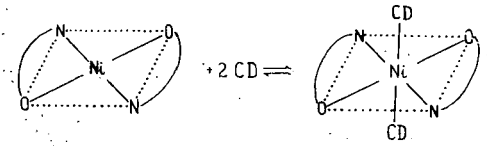
Table VIII

Equilibrium constants and thermodynamic data of the diamagnetic/paramagnetic equilibrium with various aliphatic and aromatic amines

| Amine | T | log K | $-\Delta H$ Kcal/Mol | $-\Delta G$ Kcal/Mol | $-\Delta S$ cal/deg. Mol |
|---|---|---|---|---|---|
| Quinoline | 283 | —0,78 | | | |
| | 298 | —0,86 | 2,27 | —1,18 | 11,58 |
| | 313 | —0,95 | | | |
| α-Picoline | 283 | 0,30 | | | |
| | 298 | —0,11 | 7,76 | —0,09 | 26,56 |
| | 313 | —0,36 | | | |
| Pyridine | 283 | 2,38 | | | |
| | 298 | 2,07 | 8,64 | 2,79 | 19,56 |
| | 313 | 1,74 | | | |
| n-Amylamine | 283 | 2,87 | | | |
| | 298 | 2,69 | 6,63 | 3,60 | 9,21 |
| | 313 | 2,39 | | | |
| n-Buthylamine | 283 | 3,12 | | | |
| | 298 | 2,72 | 8,28 | 3,77 | 15,37 |
| | 313 | 2,50 | | | |
| Ethylenediamine | 283 | 5,26 | | | |
| | 298 | 5,16 | 1,98 | 7,05 | —17,29 |
| | 313 | 5,11 | | | |
| Trimethylenediamine | 283 | 5,61 | | | |
| | 298 | 5,43 | 4,55 | 7,41 | — 9,56 |
| | 313 | 5,27 | | | |
| Diethylenetriamine | 283 | 5,40 | | | |
| | 298 | 5,30 | 2,03 | 7,24 | —17,43 |
| | 313 | 5,25 | | | |
| Triethylenetetramine | 283 | 5,78 | | | |
| | 298 | 5,77 | 0,27 | 7,86 | —25,47 |
| | 313 | 5,76 | | | |

group sterically hinders the bonding of the picoline molecule. If the bonding does take place then it will result in a strong distortion of the complex molecule.

In the cases of pyridine, α-picoline, chinoline, *n*-buthylamine and *n*-amylamine the equilibrium can be schematically demonstrated as follows:




(2)

Thus, a distorted six-coordinated molecule will form with $D_{2h}$ symmetry.

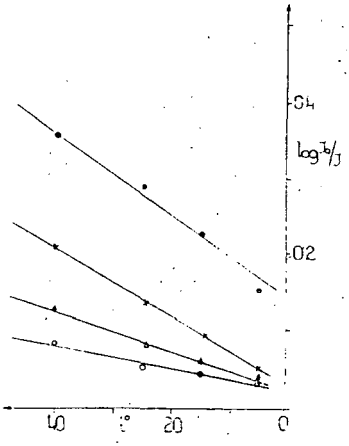



*Fig. 13.* $\log I_0/I$ values of the equilibrium solutions *vs.* temperataure.

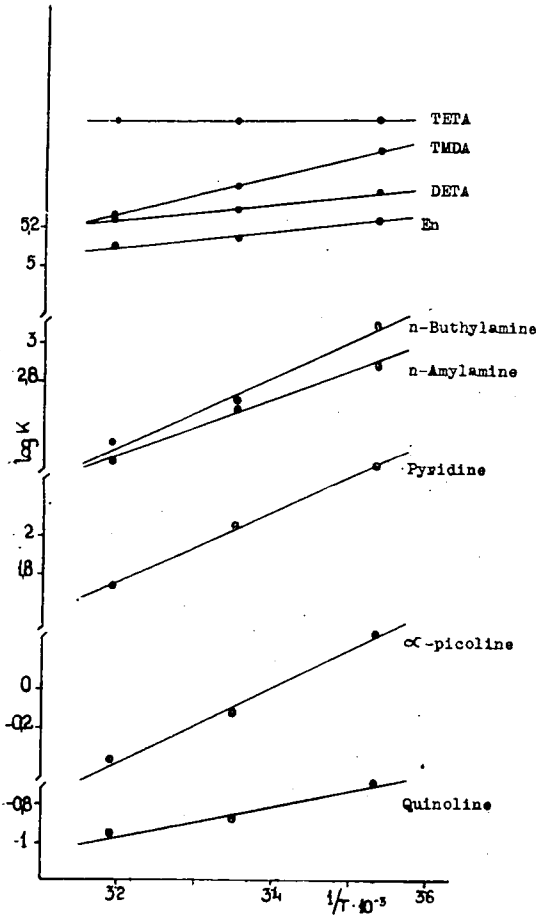



*Fig. 14.* Relation between log$K$ and $1/T$ value

It the case of these amines the adduct could be isolated in more or less crystalline form and the elementary analysis also supported the assumed composition.

The interpretation of the structure of the polyamine adducts is more difficult. At these compounds two, three and four *N*-atoms can form bonds, but their role and the mode of their coupling is not yet clearly explained on the basis of investigations hitherto. By carrying out equilibrium measurements in the same manner, constant was obtained using the formula appliep with the monoamines. For the interpretation of this fact two possibilities must be taken into consideration. First, that $NiSAOx_2$ is coupled by two amine molecules in trans position, therefore, one or more $NH_2$-, and NH- group will remain unbounded. Secondly, that by means of the remaining free amino groups the alkyl-amine chain can bound further complex molecules, thus a polynuclear structure will be formed. According to our assumption the first possibility is more likely. This is supported by the observation, that with these polyamines the adduct cannot be isolated, since the product in every case is a noncristallizable oil.

The extinction measurements at various temperatures showed the validity of BEER's law. There is no cause, therefore, to assume, that in the case of $NiSAOx_2$ a dimer/monomer equilibrium also exists besides the already mentioned diamagnetic/paramagnetic equilibrium [32, 33].

3.2.2. *On the basis of magnetic measurements*

The authors attempted to follow the diamagnetic/paramagnetic equilibrium also by susceptibility measurements. The complex is diamagnetic in chloroform while in pyridine it is paramagnetic with 3,18 BM. This value is in good agreement with the 3,2 BM found in the literature and which is equal to the observed moment of the normally paramagnetic nickel compounds.

From the susceptibility data the calculation of the equilibrium constant was attempted as follows.

In a mixture solvent of a given composition the following components must be taken into consideration:

1. chloroform,
2. $Py_f$ = the free pyridine,
3. $C_f$ = the free $NiSAOx_2$ molecule,
4. $C_bPy_b$ = the adduct contains bounded complex ($C_b$) and bounded pyridine ($Py_b$).

From these

$$Py_b + Py_f = \text{known} \quad \text{and} \quad C_b + C_f = \text{known}. \tag{3}$$

The ratio of the $C_b$ and the $Py_b$ in the adduct is

$$C_b : Py_b = M_C : 2M_{Py} \tag{4}$$

where $M_C$ and $M_{Py}$ denote the mole weight of the complex and the pyridine, resp. The susceptibility of the solution is

$$\chi_g^{\text{solution}} = \frac{m_{CHCl_3} \cdot \chi_g^{CHCl_3} + Py_f \cdot \chi_g^{Py} + C_f \cdot \chi_g^{C} + (Py_b + C_b) \cdot \chi_g^{C_b \cdot 2Py_b}}{m_{CHCl_3} + Py_f + C_f + Py_b + C_b} \tag{5}$$

where $m_{CHCl_3}$ is the amount of chloroform expressed in $g$; $\chi_g^{CHCl_3}$, $\chi_g^{Py}$, $\chi_g^{C}$ and $\chi_g^{C_b \cdot 2Py_b}$ are the $g$-susceptibilities of the chloroform, pyridine, $NiSAOx_2$ and adduct, resp. The unknown $Py_f$, $C_f$, $Py_b$ and $C_b$ can be calculated by means of the previous four equations. The equilibrium constants so calculated are summarized in Table IX.

Table IX

| No. | $\chi_g^{\text{soln.}} .10^{-6}$ | $K^*$ |
|---|---|---|
| 1 | −0,50079 | 198,20 |
| 2 | −0,49225 | 150,03 |
| 3 | −0,48723 | 145,25 |
| 4 | −0,47045 | 142,69 |
| 5 | −0,47842 | 131,26 |
| 6 | −0,46712 | 113,00 |
| | | $\bar{K}$ = 146,74 |

* T = 293 K°; $\chi_g^{CHCl_3} .10^{-6} = -0{,}488$; $\chi_g^{\text{pyridine}} .10^{-6} = -0{,}623$; $\chi_g^{\text{complex}} .10^{-6} = -9{,}947$; $\chi_g^{NiSAOx_2 \cdot 2Py} .10^{-6} = +8{,}954$

From the results two conclusions can be made. First, that the calculated equilibrium constant is in good agreement with the one, determined spectroscopically. This proves that the course of the reasoning and the calculation is right and the discussed equilibrium can also be studied by susceptibility measurements. This finding especially holds in the case of such complexes and solvent where the difficulties of solubility do not interfere with the preparation of the solution of the required concentration.

Secondly, it can be stated, that the $K$ values calculated from susceptibility data have a small, but a definite course within one series of measurement. This can partly be interpreted by the fact that, when making more precise calculations, in all probabilities, the first step must be taken into consideration.

## 4. Experimental

### 4.1. *Preparative work*

To 25 g salicylaldehyde (d: 1,1669) dissolved in 215 ml 2 *M* NaOH 12,05 g $NH_2OH.HCl$ was given. After 30 minutes of heating over a waterbath the mixture was acidified with acetic acid then cooled by ice. Salicylaldoxime was obtained by repeated extraction from the separated oil phase. After recrystallization white needle-like crystals were obtained. Mp.: 57 °C, identical with the literature data [34].

For the preparation of the complex, $NiCl_2.6\,H_2O$ and salicylaldoxime were dissolved in water and in alcohol, resp., in the ratio of 1:2 mole. The mixture was buffered with $CH_3COONa$ and slightly heated for about 10 minutes. The row product was filtered, recristallized from chloroform and identified on the basis of the absorption spectrum of its chloroformic solution.

### 4.2. *Spectroscopical work*

The electronic absorption spectra were measured by a BECKMAN DU spectrophotometer at room temperature employing 1,00 and 0,10 cm silica cells. The solvents were purified as given in the literature [35]. The reflectance curves were measured using the standard reflexion accessories and MgO as a diluent and as reference. The $f(R)$ values were calculated on the basis of the KUBELKA—MUNK [36, 37] function.

The i.r. spectrum of SAOx and $NiSAOx_2$ was determined with a ZEISS UR automatic infrared spectrophotometer with the KBr disk method*.

### 4.3. *Equilibrium measurements*

For equilibrium measurements, solutions of identical concentration were prepared in appropriate amine and chloroform and the two solutions were mixed in the required proportion at the given temperature. Six mixtures of different proportion were prepared for every series, and their extinction were measured at 620 mμ. The equilibrium constant was calculated with the Eq. 6.

$$K = \frac{1-a}{a.(\text{amine})^2} \tag{6}$$

Data of the Tables were obtained as the mean average of the $K$ values calculated in the above manner. The $\Delta H$, $\Delta G$, and $\Delta S$ values were obtained by

$$\Delta H = \frac{2{,}303.R.T_1.T_2(\log K_2 - \log K_1)}{T_2 - T_1} \tag{7}$$

and

$$\Delta G = -2{,}303.R.T.\log K = \Delta H - T\Delta S \tag{8}$$

equations, resp.

### 4.4. *Magnetic measurements*

Magnetic susceptibility measurements were performed with a WEISS type magnet in inhomogeneous magnetic field at room temperature by the GOUY method.

* The authors are grateful to DR. J. HIRES for the i. r. measurements.

An evacuating tube of 18 cm length and 6 mm inner diameter was used to hold the samples. The susceptibility of the solutions was calculated with the

$$\chi_g^{\text{solution}} = \frac{2.l.\Delta q}{m.H^2.1{,}019} \tag{9}$$

Eq. 9, where $l$ is the height of the liquid column in cm, $\Delta q$ is the change of weight in mg, $m$ is the weight of the solution in $g$, $H$ is the field-strength, and 1,019 is the din → mg conversion factor.

The $g$-susceptibility of the dissolved material was obtained by the formula

$$\chi_g^{\text{complex}} = \frac{100.\chi_g^{\text{solution}} - (100-p)\chi_g^{\text{solvent}}}{p} \tag{10}$$

where $p$ is the % concentration of the complex. The value of $\mu_{\text{eff}}$ was calculated by Eq. 11,

$$\mu_{\text{eff}} = 2{,}84(\chi_M^{\text{corr.}}.T)^{1/2}, \tag{11}$$

after the correction of the $\chi_M$ values with the PASCAL [38, 39] constants.

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## О ХИМИИ САЛИЦИЛАЛЬДОКСИМА-НИКЕЛЯ(II)

*Й. Часар и Й. Сегхальми*

Авторами изучались спектры раствора и отражения комплексов салицилальдоксима и диамагнетного, в плоскости квадратного никеля.

В индифферентном растворителе электронвозбужденный адсорпционный спектр комплекса имеет структуру характерную на диамагнетичные соединения никеля(II), а в координирующих растворителях структуру подобную парамагнетным соединениям. Из раствора моноаминов аддукт $NiSAOx_2 \cdot L_2$ был изолирован со значениями 3,16—3,22 ВМ.

В совместном растворе индифферентных и координирующих растворителей получается равновесие зависящее от температуры. Константа этого легко вычисляется из данных спектроскопии и магнетной восприимчивости. Установлено, что константы равновесия изменяются подобно как сила основ координирующих растворителей.